iron. "Graphite carbon exerts an influence only on iron in so far as it diminishes the continuity of the iron molecules. We often meet with the incorrect statement that the influence of carbon on pig-iron is quite different from its action on steel and malleable iron.

"It is easy to prove to the contrary if we distinguish properly in pig-iron between the combined carbon and that which is only mechanically incorporated as graphite, which ought not to be included in the calculation if we wish to form a judgment on the properties of pig-iron as dependent on its contents of carbon."

As one understands this, the same applies to steel.

So far there can be no difficulty in assuming at least the probability of the solution of carbon in iron, and that the physical qualities of the metal are determined by the quantity of carbon in solution, *i.e.* Akerman's hardening carbon.

The facts, *per contra*, appear mainly to indicate that carbon is merely sparingly soluble in iron at temperatures below its fusion-point.

A more serious objection (previously referred to) is that carbon is practically infusible, more especially in the graphitic form. How this intractable body so readily interpenetrates iron is a problem not easily solved.

The ordinary chemical theory of solution as usually understood does not, however, seem applicable on the whole; but some of the results accruing from the recent development of the gaseous, or rather physical theory of solution, may be made available for this purpose.

The Physical or Gaseous Theory of Solution.

In cases of simple solution the dissolved substance may be regarded as being evenly distributed throughout the solvent. The substance is dissolved by virtue of osmotic pressure, and Van 't Hoff has shown that osmotic pressure in solutions corresponds to gaseous pressure in space.

Further, it appears that both Boyle's and Charles's law holds good, at least for dilute solutions, osmotic being the equivalent for gaseous pressure, which pressure increases for constant volume proportionally to the absolute temperature. It has been, however, objected that Boyle's law is not strictly applicable to "more especially concentrated solutions," but Prof. Orme Masson (NATURE, February 1891), states that these are comparable with the case of gases at high pressures. Again, exceptions are claimed under the law of Avogadro, *i.e.* equal volumes of gases contain equal numbers of molecules under like conditions of temperature and pressure, but as regards compound gases exceptions occur, as also with dilute solutions.

Exceptions can be explained by the theory of dissociation. The analogy between gases and the physical theory of solutions thus seems complete, and Ostwald describes an experiment indicating the existence of free ions in a dilute solution of potassium chloride; other instances might also be quoted.

The author's object, however, is not to discuss the absolute correctness or otherwise of the theory of gaseous solution, which seems pretty well established; but to show that it may be applicable to the solution of carbon in molten, semi-fluid, or even merely heated iron, apart from possible cases of dissociation and chemical combinations. Solution is simply the even distribution of one body in another, or such distribution as that of permanent gaseous matter through space. It may be urged that the theory is not applicable to semi-fluid or merely heated iron. No definite line can, however, be drawn; it is obvious that the different grades of temperature are simply approximations, more or less, to the ideal fluid condition. The law of solution, as above defined, may suffer modifications, but need not in consequence be rejected.

"*Definition of Osmotic Pressure.*[1]

"Osmotic pressure is really a definite force. With suitable apparatus this force can be measured, in centimetres of a mercury column, and Pfeffer has shown that this, the osmotic pressure, is intimately connected with the nature of the dissolved substance.

"The pressure was found to be dependent on, and in proportion to, the concentration of the solution; the pressure at a specified concentration is dependent on the temperature—a rise in temperature corresponds to an increase in pressure.

"This discovery remained unnoticed. In the first instance the facts were only required for the elucidation of certain physiological questions.

"And it was not until 1886 that Van 't Hoff developed a theory of solution based on these phenomena.

"Osmotic pressure is a specific property of the substance in solution, and in this respect resembles gaseous pressure. The analogy between the state of solution and the gaseous state is clearly shown (pp. 115–17). Dissolved substances exert the same pressure in the form of osmotic pressure as they would exert if they were gasified at the same temperature without change of volume.

"All that we know of gases holds good for solutions, substituting osmotic for gaseous pressure.

"Osmotic pressure is, in some instances, very great."

And it seems clear that osmotic pressure is not a mythical, but a real or actual force of considerable power, and one which may be rationally applied to the elucidation of the cause of the carbonization of iron; further, it may even afford a clue to the phenomena observed in the production of other alloys.

As regards the carburization of iron, the physical theory of solution, "founded on the identity of osmotic with gaseous pressure," seems the only one capable of affording a satisfactory explanation of the facility with which carbon combines with iron. The chemical, or old, theory of solution apparently fails to do this. The same may be said of the assumption that chemical combinations of iron and carbon are formed. Although it must be granted such combinations may exist, yet, in the author's opinion, complete proof is still wanting. It is really difficult to realize, when dealing with stable bodies like iron and carbon, how their union can be thus accomplished.

On the contrary, the application of the law of osmose renders the conception of the transfer of carbon to iron very easy. This force, exerting probably almost illimitable power in nature, seems the only one capable of overcoming the *inertia* of bodies; such, for instance, as that of iron and carbon.

The physical theory of solution has hitherto only presumptively herein been applied to the solution of solids in liquids; and it may be asked, Is it applicable to the case of the solution of solids in solids, such as carbon and iron, when heated?

To this one can reply with confidence that the absolute solid has no existence. Unless we reject the atomic theory, it is evident that no tangible mass of matter can be termed a solid: it is an agglomeration of atoms. Further, accepting the definition of what is termed the atomic volume—*i.e.* the space occupied or kept free from the access of other matter, by the material atom itself, together with its investing sphere of heat—it follows that the atoms must be apart from each other in the so-called solid mass, and the distances between the atoms are probably considerable as compared with the actual volume or size of the atoms themselves. Therefore, there can be no difficulty in conceiving that osmotic pressure plays a part in the case of a mass of matter, "conventionally termed a solid." It is only a question of degree; the quantity of matter dissolved in a given time is simply a function of the temperature applied, and at a low temperature, the effective osmotic pressure in the case of solids seems comparable to that of a liquid evaporating under pressure of its own vapour. Evaporation is retarded, and the analogy may hold good in the case of the conventional solid.

JOHN PARRY.

PHOTOMETRIC OBSERVATIONS OF THE SUN AND SKY.[1]

ATTEMPTS have been made by Clausius and various other mathematicians to calculate the light at different points of the perfectly clear sky, and to compare the light of the whole (or a portion) of the sky with that of the sun. The difficulties of photometric measurement have prevented any of the theories being thoroughly established by experimental verifications.

In the first period of photography, it became a matter of practical importance to have some way of testing roughly the "actinic activity of diffused daylight," in order to obtain a guide for the time of exposure. Very many photographers, in those days when the evils of over-exposure could not be corrected in the printing, must have exposed a scrap of sensitive paper, and thence concluded how many seconds' exposure they would allow.

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[1] Ostwald, "On Solution."

[1] "Photometric Observations of the Sun and Sky," by Wm. Brennand. Proceedings of the Royal Society, vol. 49, n. 288, April 18, 1891, pp. 255-280.

From this point it would be a very easy step to test the "actinometric effect on sensitized paper" ("chemical action" of Roscoe) of different skies, or of the sun at different altitudes. It is not probable that the chemical action is simply proportional to the light; but it would be soon found that the "chemical action" could be much more accurately measured than the light.

Sir Henry Roscoe (partly in junction with Bunsen and with Thorpe) made many investigations and various publications between 1859–70 on the chemical action of the sun and sky as measured by its effect in darkening photographically sensitized paper. Roscoe delivered the Bakerian Lecture in 1865, "On a Method of Meteorological Registration of the Chemical Action of Total Daylight."

Throughout his investigations Roscoe pursued a direct method of experiment: he elaborately investigated a method for obtaining always paper of standard sensibility; he devised a plan for obtaining a light of standard intensity; he then exposed a piece of the paper to the action of the sky, or of sun and sky, or of a portion of the sky, and compared the effect produced in a given number of seconds with that produced in the same paper in the same number of seconds by his standard light. Roscoe also, by a laborious method, verified his fundamental asumption that light of intensity 50 acting for 1 second has the same effect as light of intensity 1 acting for 50 seconds.

Roscoe took half-hourly readings at Manchester, and thence gave the (comparative) actinic effects of the sky at different seasons of the year. Also he compared the chemical intensity of total daylight at Kew and Para, and investigated the relation between the sun's altitude and the chemical intensity of total daylight in a cloudless sky. By total daylight Roscoe meant the chemical action produced by the sun and whole sky together on a piece of paper exposed horizontally.

Roscoe found that his readings were enormously affected by the cloud-haze or invisible vapour in the air in England; he got his results, as to comparison of the chemical intensity at different seasons of the year, and at different altitudes of the sun, by assuming that in the average of a large number of observations, the effects of cloud, &c., would be self-destructive.

Roscoe found that the "chemical effect" of the sun depended only on his altitude (in a cloudless sky), being the same at Para and at Kew. He got very anomalous results as to the effects in spring and autumn in England, probably because the effects of cloudiness were not self-destructive in his series of observations. He arrived, by "averaging" the cloud irregularities, at the law that "the relation between the sun's altitude and the chemical intensity of total daylight is graphically represented by a right line" (a result only a rough first approximation to the truth). Roscoe obtained small result in comparing the chemical action at different points of the same sky, partly because he could make no experiments in person on a tropical clear sky, partly because to note these differences requires superior instruments to the direct experiment method alone tried by Roscoe.

Mr. W. Brennand was engaged at Dacca in observations, parallel to those of Roscoe, and nearly contemporaneous, 1861–66. Brennand was quite unaware of Roscoe's experiments. Being an amateur photographer, and his own photographic chemist, he was first led to devise an instrument for testing the chemical action of sun and sky, in order to obtain guidance for the number of seconds to expose a photographic plate. He was soon led on to investigate the effect of the sun at different altitudes, the effect of the sky for different altitudes of the sun, and finally the law of distribution of the "chemical action" in a perfectly cloudless sky.

Brennand's procedure in experiment differed fundamentally rom Roscoe's in two points:—

(1) Brennand only attempted observation in the cold weather at Dacca when he had a complete horizon of clear sky. He was thus enabled to carry his investigations into the laws of chemical action in a cloudless sky much farther than Roscoe, 90 per cent. (at least) of whose observations were obscured by cloud irregularities that could not be allowed for.

(2) Instead of Roscoe's direct method of observation, Brennand was early led to devise an instrument (the water-motion actinometer (see NATURE, January 8, 1891, p. 237), by the aid of which he was independent both of the standard light and standard paper attained by Roscoe with so great labour. The sun himself was, in fact, Brennand's standard light, and the darkening of each paper was read as a ratio; for instance, if an exposure of 10 seconds to sun and sky produced the same tint in the paper that was produced by the sun alone in 17 seconds, then the effect of the sun alone was reckoned $\frac{10}{17}$ of the sun and sky together. It is clear that *any* uniform paper should give such ratios the same, though the actual shades produced would be different in different papers. All the papers made by Brennand himself were found "uniform," *i.e.* to within the limits of variation (say, 2 per cent.) within which the darkened paper can be read, *i.e.* the shades can be matched. Any good photographic paper is found uniform enough for the purpose; but some of the ordinary photographic papers tried lately in England have been found not good enough; the nature of the irregularities introduced by imperfect paper is such as to suggest very soon their cause.

It is to be noticed that all that can be observed is a ratio: the observations in Roscoe's direct process are not absolute. In that process there is a standard unit, viz. the blackness produced in the standard paper by the standard light action at the unit of distance for n seconds. Any other light that produces this blackness has the numerical value $\frac{x}{n}$ in Roscoe's unit. There is little doubt but that Roscoe got his standard light and standard paper, each time he recovered them, correctly within the percentage of error involved in the reading. He would be certain to have prepared his salts of exactly the proper strength; but there is an element of uncertainty in the degree in which papers apparently of similar texture and in a similar state of dryness, &c., take up salts. This element of uncertainty is avoided by Brennand's method, which is far more absolute than Roscoe's.

The water-motion actinometer gave Brennand, for each observation, a shaded strip darkened gradually from 0 to 8 (or to 16) seconds. He could note on this the point at which a particular unit of darkening was produced, and the inverse of this time gave him a measure of the ratio of the observed "chemical action" to that which had produced the unit darkening.

This, of course, involved the assumption that light of intensity 50 acting for 1 second has the same effect as light of intensity 1 acting for 50 seconds. This Brennand thought might be assumed; but he proved it in the following very simple manner.

A slip of sensitized paper is formed into a ring (a short cylinder) and placed round a light (the wick of a candle was used, but any light would do, irregular or not) excentrically. After a certain time the slip is examined and found to be shaded gradually from the farthest to the nearest point, the effect at each point varying inversely as the square of the distance.

Thus if A be the source of light, O the centre of the ring, and if we have $\mathrm{OB} = a$, $\mathrm{OA} = b$, $\mathrm{POB} = \theta$, we shall have the chemical effect at any point P of the slip vary as

$$\frac{1}{\mathrm{R}^2} = \frac{1}{\mathrm{AP}^2} = \frac{1}{a^2 + b^2 - 2ab\cos\theta}.$$

In a particular experiment Brennand took $a = 1{\cdot}4$ inch, $b = {\cdot}4$ inch.

$$\cos^2\frac{\theta}{2} = \frac{3{\cdot}24 - \mathrm{R}^2}{2{\cdot}24}.$$

Taking the unit of intensity that at the distance 1 inch from the wick, and calculating the values of θ for values of the intensity 1, ·75, ·5, and ·3, we have $\theta = 0, 20^\circ\ 10', 78^\circ\ 34'$, and $141^\circ\ 48'$ respectively. The lengths of arc corresponding to these are found to be ·49 inch, 1·92 inch, and 3·45 inches respectively. These lengths can be marked off on the slip. Another slip can then be darkened in the water-motion actinometer, by any light; a unit can be marked on this slip at the point where the shade corresponds with that at the unit in the ring slip; it then can be seen whether the intensity of shade at the distance ·49 on the ring slip agrees with that at three-fourths the time for unit on the actinometer slip; and similarly for the other calculated values. This experiment verifies the law assumed, and moreover affords a check on the paper employed, and on the closeness with which tints can be matched.

Another important means of verification was employed by Brennand, which Roscoe does not appear to have availed himself of. Calling the effect of the sky alone in darkening paper B, and the effect of the sun and sky together A, Roscoe observed A and observed B, and then calculated the effect of the sun alone as A − B. Brennand did this; but also observed the sun alone by the simple device of a vertical slit in a shutter, and was thus able to check the accuracy of his method and of his work.

Having thus established the trustworthiness of his *modus* *operandi*, Brennand, with his water-motion actinometer, drew up, by an ample series of observations extended over several years, the Table B given in NATURE (January 8, 1891, p. 237). The numbers in this table are ratios, and they may be all multiplied by any number without any real alteration in the table. The unit of chemical action originally started with was the blackness produced by 100 grains of a candle burnt at the unit of distance; and this is the unit which underlies Table B. Brennand early found, as Roscoe found, that the sun has always the same effect at the same altitude in a perfectly clear sky. Hence, in all the later observations the unit was recovered from the sun.

Thus, to take a series of observations, with the water-motion actinometer, with strips of an unknown (but uniform) paper: first, a strip is placed in the instrument, the sun alone being admitted by the vertical slit, and the sliding shutter is run up; we thus get a gradually tinted slip beside the gauge marked in seconds. The altitude of the sun is noted; suppose it 30°; the number in Table B for this altitude is 0·1070, *i.e.* the number of seconds which produces unit darkening by sun alone at this altitude is $\frac{1}{0{\cdot}107}$ seconds $= 9\frac{1}{3}$ seconds. Then on the sun strip a mark is made opposite the 9⅓ seconds graduation on the gauge; this is the unit blackness for the paper, and any subsequent strip exposed is "read" by marking the point on it which has the same blackness.

This method of recovering the unit is not sufficient to determine, for instance, whether the sky in England on a certain morning was really clear, *i.e.* as truly clear as the Dacca cold-weather sky. To determine this particular point, Brennand lately in England burnt 100 grains of a candle (as near as he could get) similar in composition to his Dacca candle, and the result shows conclusively, by the exact accord of several observations lately made near Taunton with corresponding old observations at Dacca, that in this case the two candles must have produced equal effects. But it is obvious that the candle could only be trusted by these results. The experiments made with the candle were not made to recover the Dacca unit, but to test the candle. The exact agreement in the several results raises the very strongest presumption that the Taunton candle was equal to the Dacca candle. It is, however, possible that the Taunton sky varied for the several observations in exact ratio with a variation in the Taunton candle; and it can only be said that Brennand's observations on this particular point, so far as they go, support Roscoe's result that the chemical action of the sun is the same at the same altitude in a perfectly clear sky, always and everywhere.

When the chemical action of the sky (or of some portion of it) on a piece of flat paper is observed, what is measured is the integral of the resolved effects of each sky element. Thus if, as in Roscoe's experiments, the piece of sensitized paper is exposed horizontally, and the effect of the whole sky (the sun being stopped off) is taken, we have the total effect of a ring of the sky distant θ from the zenith to be multiplied by $\cos\theta$, and then the effect of all such rings from the zenith to the horizon to be summed. This view of the resultant action suggested to Brennand the more original branch of his investigations. He was early led to suspect that the chemical action of the sky varied in different parts of it. He devised an instrument, which he calls the mitrailleuse actinometer, by which he was enabled to prove that the chemical action of the sky is a minimum in the great circle distant 90° from the sun; for an altitude α of the sun this minimum he calls i_a. Brennand then further proves that the chemical action (at the same time) at any other point of the sky distant θ from the sun is then $i_a \operatorname{cosec} \theta$.

Having established these important laws, Brennand is able, by mathematical process, having i_a given him, to calculate the total effect of any defined portion of the sky on a plane of sensitized paper exposed at any given angle. He was thus enabled to compare Roscoe's readings of total diffused daylight on paper exposed horizontally with his own Dacca readings on paper exposed perpendicularly to the direction of the sun.

These investigations led Brennand to a theoretic value for the duration of twilight, and to the devising a new instrument, the "octant actinometer," by which the fundamental constant i_a can be observed directly.

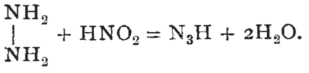
This "octant" actinometer observes one-eighth of the heavens, cut out by three planes at right angles to each other, placed so that the line OS, the intersection of two of the planes, passes through the sun. Owing to the cloudy skies of Taunton, Brennand (who experiments only with a clear sky) had been able very imperfectly to test this instrument at the time his paper was read to the Royal Society. He has since found that this "octant" may be turned in any way round OS (above the horizon, of course) without altering the reading on either of the three planes of the octant. This "octant," therefore, only requires one-fourth of the visible hemisphere round the zenith to be clear, for a good observation. What is more important, it enables the observer, when the sky is clear, and the sun's altitude from 30° to 60°, to take an observation of a part of the sky entirely 30° from the horizon; so that the uncertainty arising from haze near the horizon (which could not before be allowed for) may by this capital instrument be avoided, and i_a obtained without any integrations or calculations beyond division by a number.

In the whole of these later developments, Brennand's work is entirely original. Sir Henry Roscoe, following a somewhat different course of inquiry, has made experiments on the chemical action of the sun and sky at different levels above the sea; and on the total effect during different months or seasons of the English sky with all its cloud, fog, and smoke; which last is an important practical measure of the climate in its influence on vegetation, and perhaps on human health.

The researches of Roscoe and Brennand have thus, though overlapping at particular points, extended mainly in different directions. Brennand, in the ground covered by both, puts forward far the more accurate determinations; his table (B) given in NATURE, January 8, 1891, p. 237, professes to be of the same character and value as a table of the constants of refraction,—Brennand has had half a century's experience with the chemistry of photographic paper, and is an excellent mathematician of the old school. Moreover, the three leading actinometric instruments he has devised, the water-motion, the mitrailleuse, and the octant, show him to be possessed of much resource in devising instruments of research.

INORGANIC SYNTHESIS OF AZOIMIDE, N_3H.

A METHOD of synthesizing this interesting compound of nitrogen and hydrogen, by means of a simple reaction involving only purely inorganic substances, has been discovered by Prof. Wislicenus, and is described by him in a communication to the current number (No. 12) of the *Berichte* of the German Chemical Society. The reactions by which azoimide has hitherto been obtained have all been of an organic nature, and more or less complicated. The mode of preparation described by its original discoverer, Prof. Curtius, in reality depends upon a very simple reaction, that of nitrous acid upon hydrazine, N_2H_4, the other hydride of nitrogen whose preparation we also owe to Prof. Curtius,

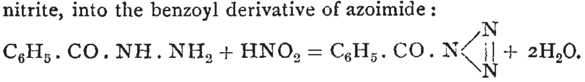


$$\begin{matrix}\mathrm{NH_2}\\ |\\ \mathrm{NH_2}\end{matrix} + \mathrm{HNO_2} = \mathrm{N_3H} + 2\mathrm{H_2O}.$$

Hydrazine, however, has only yet been prepared from its organic derivatives, and moreover it has not been found practicable to actually convert free hydrazine itself by means of nitrous acid into azoimide, only certain organic derivatives being acted upon by nitrous acid with production of azoimide. The perfected mode of preparation described by Prof. Curtius at the close of last year is very briefly as follows. Benzoyl hydrazine, $\mathrm{C_6H_5.CO.NH.NH_2}$, is first formed by reacting with ethyl benzoate upon hydrazine hydrate:

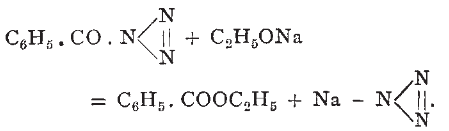
$$\mathrm{C_6H_5.COOC_2H_5 + N_2H_4.H_2O}$$
$$= \mathrm{C_6H_5.CO.NH.NH_2 + C_2H_5OH + H_2O}.$$

The benzoyl hydrazine is then converted by means of nitrous acid, obtained from a mixture of glacial acetic acid and sodium nitrite, into the benzoyl derivative of azoimide:



$$\mathrm{C_6H_5.CO.NH.NH_2 + HNO_2 = C_6H_5.CO.N}\left\langle\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}\right. + 2\mathrm{H_2O}.$$

From benzoyl azoimide the sodium salt of azoimide is next formed by treatment with sodium ethylate:—



$$\mathrm{C_6H_5.CO.N}\left\langle\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}\right. + \mathrm{C_2H_5ONa}$$
$$= \mathrm{C_6H_5.COOC_2H_5 + Na - N}\left\langle\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}\right..$$